# VI.12 High Temperature Electrochemistry - University of Florida

## Objectives

- Apply computational approach to develop fundamental understanding of ionic transport and heterogeneous electrocatalysis in SOFCs.
- Develop high resolution characterization techniques to quantify electrode microstructures.
- Combine heterogeneous catalysis, electrochemistry, and microstructure characterization techniques to de-convolute contributions to electrode polarization.

## Accomplishments

- Utilized *ab initio* and molecular dynamic simulations to calculate defect and defect cluster formation energies and effect on ionic transport.
- Computationally and experimentally determining thermo-mechanical properties based on fundamental thermodynamic/bond-energy constants.
- Used atomic-level simulation methods to elucidate the effects of non-stoichiometry and temperature on the elastic properties of $CeO_{2-x}$.
- Determined adsorption and absorption energies for O on and in $LaFeO_3$ (110) using first principles, and electronic structure calculations.
- Developed high resolution focused ion beam (FIB) - scanning electron microscopy (SEM) characterization technique and applied to SOFC cathodes to quantify 3-D microstructure.
- Developing unique electrocatalytic techniques to determine fundamental oxygen exchange kinetics (k/D) on cathode surfaces based on O-isotope exchange as a function of applied voltage/current.

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## Introduction

To fully achieve the tremendous socio-economic benefits of electrochemical energy conversion and power generation, fundamental scientific breakthroughs in the transport of ionic species through electrolyte/membranes and reaction rates at electrode surfaces are necessary. Therefore, the mission of the University of Florida High Temperature Electrochemistry Center (HiTEC) is to develop a fundamental understanding of ionic transport in, and electrocatalytic (electrochemical catalysis) phenomena on the surface of, ion-conducting materials. The research spans the range from first-principles calculations and molecular dynamic simulations of ionic transport and gas-solid interactions of novel ion-conducting materials and electrocatalysts to development of advanced technology devices for efficient energy utilization:

**SOFCs** – Increasing the ionic conductivity and electrode reaction rates results in higher power density cells at lower operating temperature. These higher power density cells will dramatically reduce the cost of fuel cell technology, thus, overcoming the final hurdle (cost) to widespread commercial deployment.

**Membranes** – Membrane reactors are a major component of the FutureGen Initiative. Improving the transport of ions through the membrane and reaction rates at the membrane surface will help achieve dramatic breakthroughs in industrial energy efficiency and cost of hydrogen production.

**Sensors** – By developing a fundamental understanding of the gas-solid reactions that occur on sensor electrodes we will be able to develop sensors that are highly sensitive and selective to specific gaseous pollutants. These sensors will allow more accurate control of combustion resulting in greater fuel economy and reduced air pollution.

## Approach

Our computational research focuses first on gaining insight into mechanisms of ion transport and heterogeneous electrocatalysis, and then on applying this fundamental knowledge to the design of new materials. Using electronic structure calculations and large-scale atomic-level simulation on cluster parallel computers we are elucidating the fundamental processes of ion transport in various electrolyte and electrode materials. Among the effects being explored are defect clustering on ionic transport and the use of doping to increase ionic transport. The effect of grain boundary interfaces is being determined from simulations of ionic transport in polycrystalline materials. The insights gained from these simulations will help guide the development of higher conductivity electrolyte and electrode materials.

In addition, we are using similar calculations to develop a fundamental understanding of heterogeneous electrocatalytic phenomena at the surface of ion-conducting ceramics. Because cathode polarization limits the performance of SOFCs at low temperature, the insights gained from this study will lead to the development of lower polarization SOFC cathodes at lower temperatures. In addition, these computational methods will be used to determine the mechanisms responsible for the cathode performance degradation.

We are developing high-resolution, quantitative, microstructural characterization techniques based on a FIB-SEM. This includes development of mathematical techniques to create a 3-D reconstruction of the entire porous electrode structure as well as to quantify electrode microstructural features (e.g., triple phase boundary length, porosity and tortuosity). In addition, we are using the FIB-SEM to prepare samples for high resolution transmission electron microscope (HRTEM) analysis of specific interfaces for analysis of issues such as tertiary phase formation, cathode degradation, etc.

Finally, using heterogeneous catalysis techniques: temperature programmed desorption (TPD), temperature programmed reaction (TPR), and oxygen-isotope exchange; combined with electrochemistry techniques: impedance spectroscopy, current-voltage (I-V), and conductivity relaxation; and the microstructural characterization and computational approach (above); we are de-convoluting the various contributions to electrode polarization to obtain a more fundamental understanding, and develop a methodology to design improved performance electrodes in the future.

## Results

**Computational** - The thermal and mechanical properties of $CeO_{2-x}$ were simulated by molecular dynamics (MD), with interatomic interactions described by a conventional Buckingham potential plus Coulombic interactions. The lattice parameter expanded with both increasing temperature and oxygen vacancy concentration (non-stoichiometry, x), consistent with experimental observations as shown in Figure 1a. The coefficient of thermal expansion for different compositions was also calculated. A detailed study of the mechanical properties was performed with the MD simulation. The elastic constants $C_{11}$, $C_{12}$, and $C_{44}$ were calculated as a function of composition ($0 \leq x \leq 0.3$) and temperature (0 - 1500 K). These values were used to obtain the bulk modulus, Young's modulus, and shear modulus for the corresponding compositions and were found to be in agreement with experimental values.

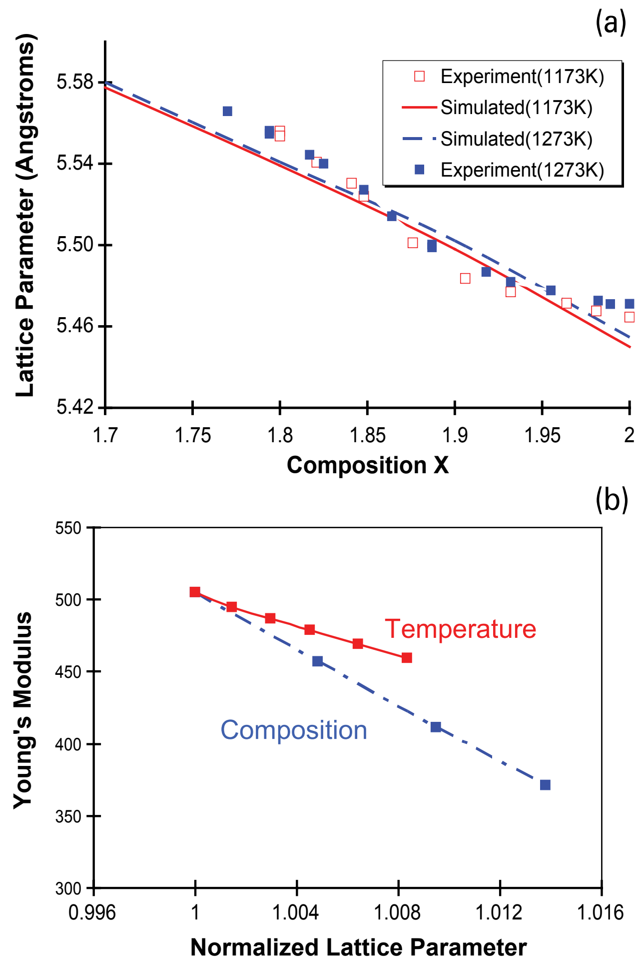


**FIGURE 1.** (a) Comparison of Lattice Parameter Between Calculated and Published Data; (b) Comparison of Young's Modulus Dependence on Temperature and Composition

The comparison between temperature and composition effects on Young's modulus (Figure 1b) indicates a greater effect due to oxygen vacancy concentration than temperature. Simulations on the oxygen vacancy diffusion mechanism are underway.

In addition, we optimized the conditions under which first principles, electronic structure calculations of $LaFeO_3$ should be carried out - *density functional theory (DFT) calculations within the generalized gradient approximation (GGA) as implemented by Perdew, Burke, and Ernzerhof (PBE), including the projector augmented wave (PAW) approximation with the Vienna Ab-initio Simulation Package (VASP)*. In our optimizations, the supercell shape and volume was free to change and all the ions were free to move to lower their total energy and decrease the forces on the atoms. The calculated values are in good agreement with experimental values and predict that $LaFeO_3$ undergoes a rhombohedral, Jahn-Teller-induced distortion in agreement with experimental data.

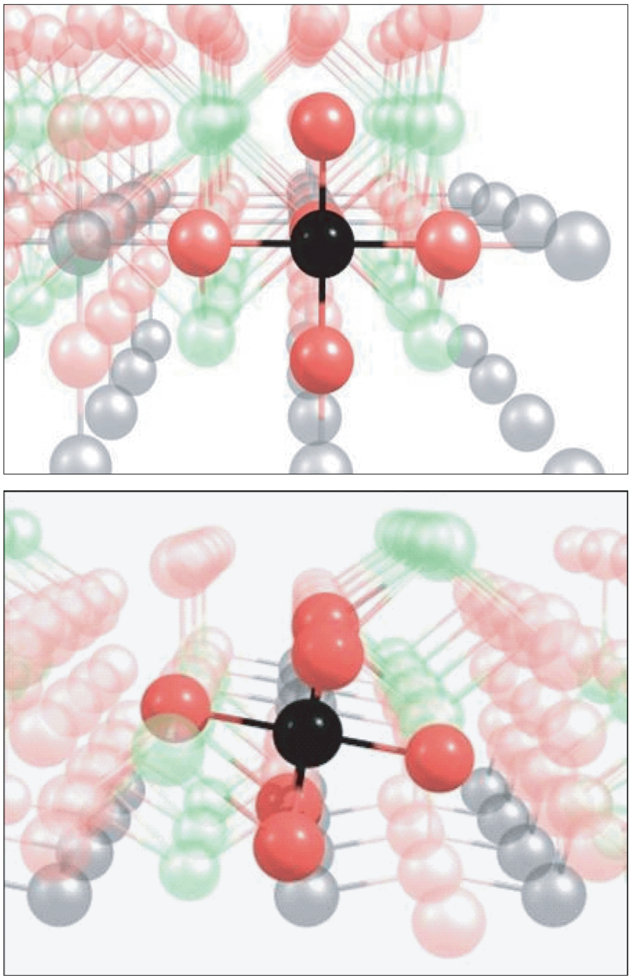

FIGURE 2. Calculated $LaFeO_3$ Bulk and Surface Configurations

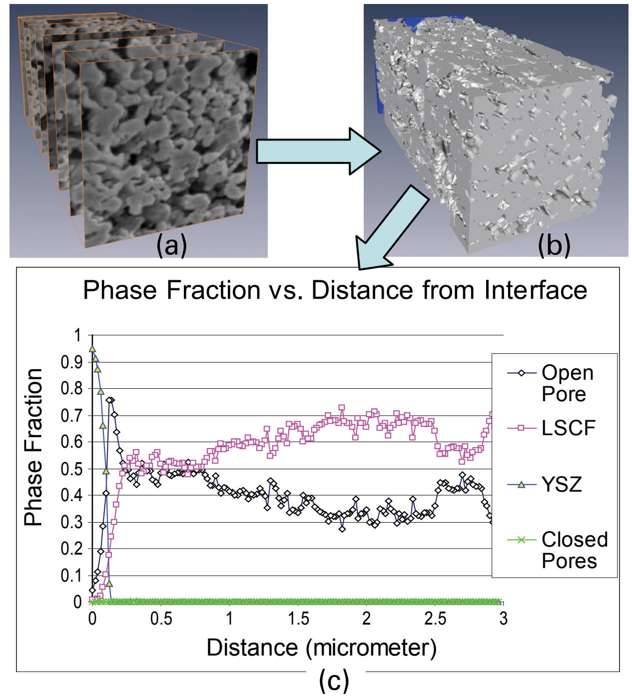


FIGURE 3. FIB-SEM serial sectioning and imaging of LSCF, conducted at ~20 nm intervals. (a) The resulting two-dimensional (2-D) images are stacked and aligned with the aid of fiducial marks.
(b) 3-D reconstruction of the serially sectioned region of interest.
(c) The reconstruction is then manipulated to quantify microstructural properties of the porous cathode such as average particle size, average pore size, closed porosity, open porosity, tortuosity, surface area, interface area, and porosity grading.

The energy of oxygen adsorption on the LaO-terminated $LaFeO_3$ (110) surface and absorption in bulk $LaFeO_3$ were calculated (Figure 2). In the case of absorption, the defect formation energy of the oxygen interstitial is determined to be 2.26 eV. The energy of adsorption is predicted to be -3.65 eV for a La-La bridge site and -3.13 eV for a La-O bridge site. Therefore, for the (110) surface the preferential mechanism is for oxygen to adsorb on a La-La bridge site. These calculations are continuing for the FeO-terminated surfaces.

**Microstructural Characterization** – The FIB-SEM was used to evaluate LSM and LSCF cathodes on YSZ. The ion beam is rastered across the region of interest (ROI) to remove material while the SEM field emission gun is utilized to image the freshly milled surface with a secondary electron detector down to a 3 nm lateral resolution (Figure 3a). After the SEM image has been acquired a subsequent section of material is ablated with the FIB and the serial process continues to the desired depth. This serial process allows us to create a fully interactive 3-D reconstruction of the electrode microstructure (Figure 3b).

The resultant 3-D microstructure is then qualitatively and quantitatively analyzed. For example, Figure 3c shows the pore, LSCF and YSZ volume fractions as a function of distance from the electrode/electrolyte interface (x=0). Moreover, using this technique on LSM/YSZ samples sintered at various temperatures we can quantify the decrease in TPB length (Figure 4a) and increase in pore size (Figure 4b) as a function of sintering temperature.

The dual beam FIB-SEM also expedites TEM sample preparation. This is done by utilizing the FIB to micromachine and micropolish sectional HRTEM samples, allowing for pinpointing ROIs such as the cathode/electrolyte interface. This was done across the LSM/YSZ interface using an HRTEM with EDS to determine nano-scale compositional changes (Figure 5) and with electron diffraction (Figure 6) to differentiate the crystal structures as a function of sintering.

**Deconvolution of Electrode Polarization** - Finally, we are using heterogeneous catalysis techniques (TPD/

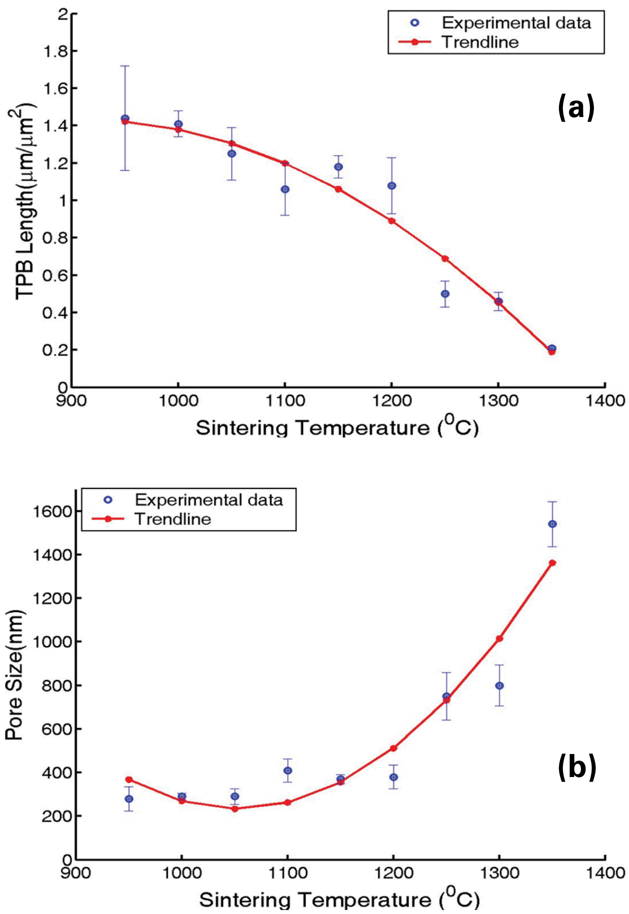


**FIGURE 4.** TPB Length (a) and Pore Size (b) of LSM Cathode as a Function of Sintering Temperature

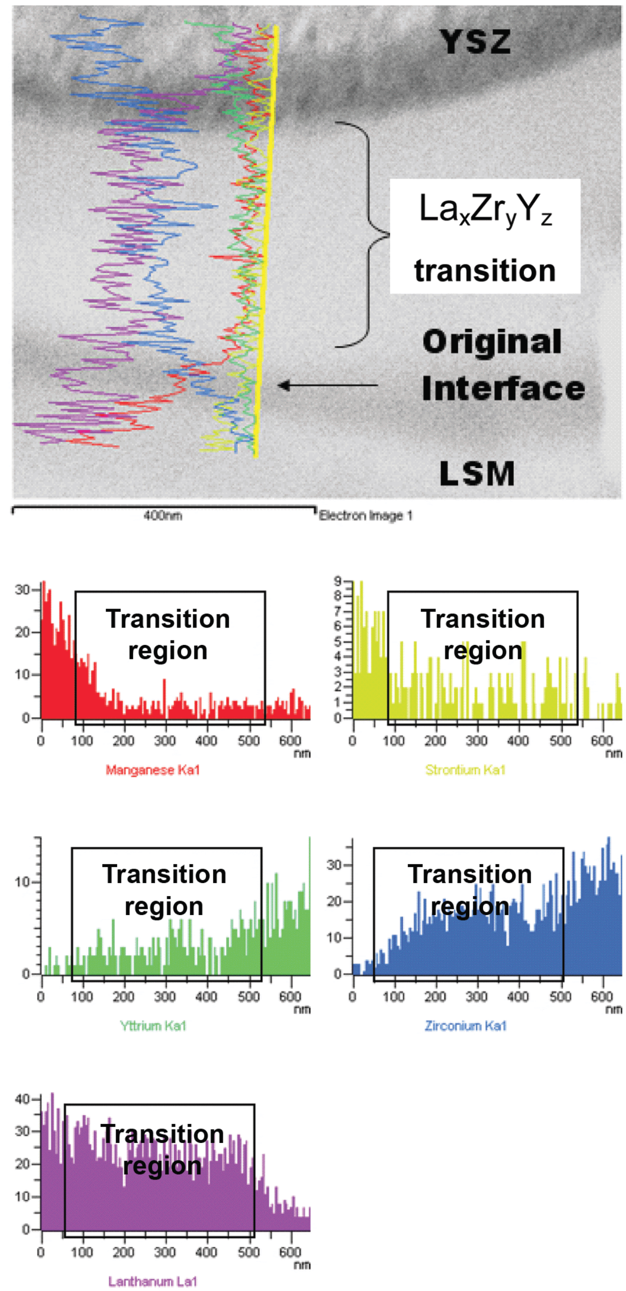


**FIGURE 5.** LSM/YSZ interface by high resolution STEM. Interface region (~350 Å wide) is distinguishable by intensity contrast. EDS analysis relates the contrast differences to changes in composition showing La diffuses into the YSZ region forming a $La_xZr_yY_z$ type interface phase.

TPR and oxygen-isotope exchange) combined with electrochemistry techniques (impedance spectroscopy, I-V, and conductivity relaxation) and the microstructural characterization and computational approaches to obtain a more fundamental understanding of the various contributions to electrode polarization.

We have set up a high sensitivity (ppb) mass spectrometer and have performed TPD and TPR experiments on LSF-based cathode materials. This has been modified to incorporate $O^{18}$ exchange experiments. We have fabricated a sample holder that allows us to do these experiments *in situ* under applied potentials and currents. In addition, we have set up and validated a conductivity relaxation apparatus and are modifying it to allow *in situ* sampling with the mass spec. The resulting apparatuses are unique in their ability to separate out surface exchange (k) and diffusion (D) coefficients and the effects of potential/current on the electrocatalytic phenomena of activation polarization.

Using impedance spectroscopy we have separated out the various contributions to polarization of LSM, LSF, and LSCF cathodes. The same samples were then analyzed with the FIB-SEM to quantitatively relate microstructure to polarization (e.g., Figure 7). As can be seen, there is a direct correlation between the impedance we attribute to dissociative adsorption and pore surface area (normalized to the cathode volume). Similar trends have been observed for charge transfer resistance and TPB length.

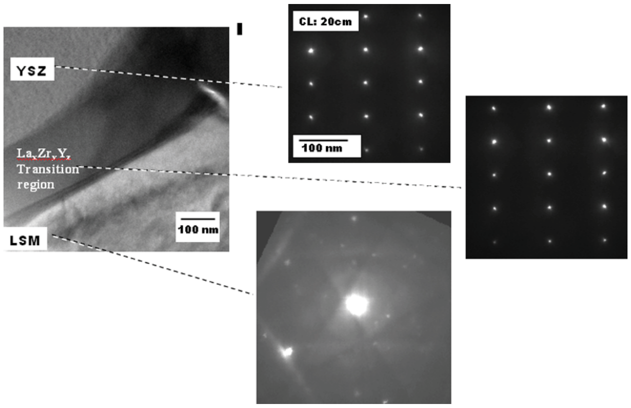


**FIGURE 6.** TEM diffraction patterns of YSZ and LSM are distinctly different. The diffraction pattern of the transition region is the same as that of the YSZ region. Similarity in the crystal structure between YSZ and the interface region suggests that the interface is formed by the diffusion of La from the LSM region into YSZ forming the transition region.

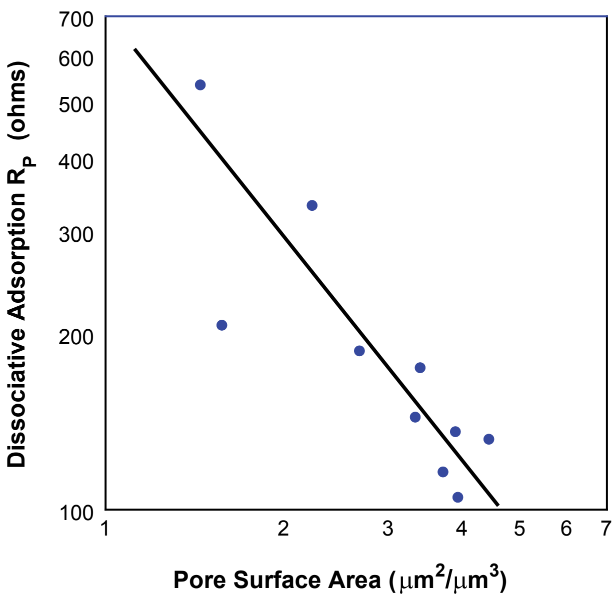


**FIGURE 7.** Relation Between Impedance (Dissociative Adsorption) and Microstructure (Normalized Pore Surface Area) for an LSM Cathode

## Conclusions and Future Directions

- Demonstrated that computational simulations of thermo-mechanical properties are consistent with experimental results, and show the importance of oxygen vacancy concentration on lattice expansion.
- Computationally determined adsorption and absorption energies for O on/in $LaFeO_3$ (110) cathodes. Results indicate preference for La-La surface sites. Calculations to continue on Fe terminated surfaces.
- Developed high resolution FIB-SEM characterization technique and applied it to SOFC cathodes. Demonstrated that results can be used to produce 3-D reconstructions. Quantification of LSM, LSF, and LSCF cathode microstructures is underway.
- Developing unique electrocatalytic techniques to determine fundamental oxygen exchange kinetics (k/D) on cathode surfaces. The resultant experimental data combined with computational results will be used to design improved cathode materials.
- Combined microstructural characterization of LSM cathodes with impedance spectroscopy results to de-convolute polarization mechanisms and quantify the effect of microstructure on electrode polarization. These experiments will continue and we will apply to LSF and LSCF cathodes.

## FY 2006 Publications/Presentations

**1.** "High Temperature Materials," K. E Spear, S. Visco, E. J. Wuchina and E. D. Wachsman, *Interface*, The Electrochemical Society, **15-1**, 40-44 (2006).

**2.** "Ionic Conduction in Zirconia Films of Nanometer Thickness," X. Guo, E. Vasco, S. Mi, K. Szot, E. D. Wachsman, and R. Waser,' *Acta Materialia*, **53**, 5161-5166 (2005).

**3.** "Schottky Barrier Formed by Network of Screw Dislocations in $SrTiO_3$," X. Guo, Z Zhang, W. Sigle, E. D. Wachsman, and R. Waser, *Applied Physics Letters*, **87**, 162105 (2005).

**4.** "The Search for a Low Temperature SOFC; How Low Can We Go?" E. D. Wachsman, Stanford University Seminar, March 24, 2006, Stanford, CA.

**5.** "Investigations Into Cathode Mechanisms and Novel Materials Development," E. D. Wachsman, UF-DOE High Temperature Electrochemistry Center Workshop on Fundamental Mechanisms of SOFC Cathode Reactions, January 27, 2006, Cocoa Beach, FL.

**6.** "Application of Computational Methods to Understanding SOFC Cathode Mechanisms", J. He, C.-W. Lee, E. Wachsman, S.B. Sinnott, M.W. Finnis, E.C. Dickey, UF-DOE High Temperature Electrochemistry Center Workshop on Fundamental Mechanisms of SOFC Cathode Reactions, January 27, 2006, Cocoa Beach, FL.

**7.** "Physical Origin of the Low Grain Boundary Conductivity of Oxygen Ion Conductors: Zirconia and Ceria," X. Guo and E. D. Wachsman, American Ceramic Society, January 22-27, 2006, Cocoa Beach, FL.

**8.** "Fundamental Studies of SOFC Materials," E. D. Wachsman, DOE - SECA Core Technology Program Peer Review Meeting, October 25-26, 2005, Denver, CO.

**9.** "Schottky Barrier Formed by Network of Screw Dislocations in $SrTiO_3$", X. Guo, E. D. Wachsman, Z. Zhang, W. Sigle and R. Waser, The Electrochemical Society, October 16-21, 2005, Los Angeles, CA.

**10.** "Ionic Conduction in Zirconia Films of Nanometer Thickness", X. Guo, E. D. Wachsman, E. Vasco, S. Mi, K. Szot and R. Waser, The Electrochemical Society, October 16-21, 2005, Los Angeles, CA.

**11.** "The Search for a Low Temperature SOFC; How Low Can We Go?" E. D. Wachsman, Montana State University HiTEC Seminar, October 6, 2005, Bozeman, MT.

**12.** "Effect of Oxygen Sublattice Ordering on Conductivity in Highly Defective Fluorite Oxides," E. D. Wachsman, American Ceramic Society, September 11-16, 2005, Maui, HI.